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(54) Title: INK-JET PRINTING COMPOSITIONS

(57) Abstract

A polyamide resin useful in the preparation of hot-melt inks for ink-jet printing is prepared by the condensation polymerization reaction of a monoacid, a second reactant selected from aminoalcohols and blends of aminoalcohols and diamines, and a diacid. Preferably, the monoacid, second reactant and diacid are reacted together in mole ratios of 2:2:1. Optionally, a monoamine or monoalcohol may be substituted for a portion of the second reactant and the diacid. The polyamides afford the ink compositions with a low viscosity at the elevated operating temperatures of an ink-jet printer, yet are solid at room temperature and contribute good adhesion to the printed substrate.

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INK-JET PRINTING COMPOSITIONS

BACKGROUND OF THE INVENTION

5 1. Field of the Invention

The present invention relates to polyamide resin-based printing compositions, and in particular to printing compositions useful for hot-melt printing inks.

2. Brief Description of the Prior Art

10 Ink-jet printing is a non-contact printing process for the printing of many substrates such as paper, films, foils and the like. Certain ink-jet printers are designed to use hot-melt, also known as "phase-change," inks. One requirement of a hot-melt ink is that it be in the solid form at room temperature and in the liquid form when contacted with the elevated operating temperatures maintained in the
15 printhead of a printer employing hot-melt inks. In printing that employs hot-melt inks, molten ink is ejected from the printhead and upon hitting the substrate, cools, and solidifies, and adheres to the substrate.

Hot-melt inks and components for hot-melt inks are disclosed, for example in United States Patent 3,653,932, which teaches the use of didodecyl sebacate as
20 a carrier for the ink.

United States Patent No. 4,830,671 to Frihart et. al. discloses a composition for use in hot-melt ink-jet printing applications. The ink comprises a colorant and a resinous binder prepared from polymerized fatty acid, a diamine and a monocarboxylic acid.

25 United States Patent No. 4,889,650 to Jaeger et. al. also relates to a hot-melt printing composition. The Jaeger ink comprises a colorant and a fatty-amide containing material in which the fatty amide-containing material is comprised of a tetraamide compound and a monoamide compound. The Jaeger ink is capable of producing thin films of uniform thickness with a high degree of lightness and
30 chroma and which are rectilinearly light transmissive.

United States Patent No. 5,085,099 also to Jaeger et. al. discloses modified hot-melt ink compatible colorants which are comprised of a hot-melt ink-soluble complex of a tertiary alkyl primary amine and dye chromophores. The dye

chromophores are materials with at least one pendant acid group in the free acid form and which absorb light in the visible wavelength region to produce color. The composition also contains a fatty amide containing material comprised of a dimer-acid linked tetraamide and optionally, a monoamide.

5 A number of patents in the prior art, including United States Patents 4,297,479; 4,684,409; 4,308,374; and 4,389,521, disclose the production of high molecular weight polyamides from equimolar amounts of diamine and diacid. These polyamides possess film-forming characteristics and are useful in the production of nylon.

10 United States Patent 4,066,585 discloses polyamide resins suitable for use in hot-melt flexographic and intaglio inks comprising polymerized fatty acid, a monocarboxylic acid and a diamine or alkanolamine.

 United States Patent 3,595,816 to Barrett discloses adhesive polyamide compositions in which hydrogenated dimer acid is reacted with amine, wherein
15 from 90-100 equivalent percent of the amine should be diamine, and the remainder of the amine may include monoamine.

 United States Patent 4,816,549 to Rumack discloses a polyamide resin composition which is made up of from 5-35 equivalent percent of a monoamine, 65-95 equivalent percent of a diamine (some of which must be 1,2-
20 diaminocyclohexane), 75-100 equivalent percent of a diacid formed from polymerizing fatty acids, and 0-25 equivalent percent of an aliphatic or cycloaliphatic diacid. The monoamine terminated compositions are disclosed as being useful as binders in solution printing inks because they are soluble in toluene.

25 U.S. Patent 2,272,466 discloses a process for the preparation of polyamides or, more specifically, diamides. The process comprises condensing a selected primary or secondary amine with a cyclic dicarboxylic acid such as terephthalic acid or isophthalic acid, where the dicarboxylic acid is characterized as being unable to form an intramolecular anhydride linkage.

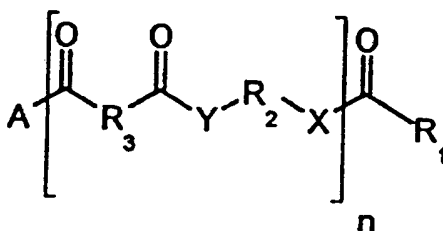
30 There continues to exist a need in the art for hot-melt ink components having the proper combination of melting point, melt viscosity, clarity, inertness, compatibility with other components, and adhesive properties which meet the commercial demands placed on these materials, especially for printing on non-porous substrates such as polyethylene, polyesters and polystyrene films.

SUMMARY OF THE INVENTION

The present invention is directed to polyamide resin compositions including novel polyamides. The novel polyamides are prepared from a reaction mixture including monoacid, a second reactant selected from aminoalcohols, and blends of aminoalcohols and diamines, and diacid ("symmetric polyamides") or including monoacid, a second reactant selected from diamines, aminoalcohols, and blends of aminoalcohols and diamines, diacid, and a fourth reactant selected from monoamines, monoalcohols, and blends thereof ("asymmetric polyamides"). The present invention is further directed to hot-melt ink compositions that incorporate the polyamide resin compositions of the present invention.

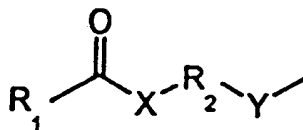
The polyamide resin composition has a low viscosity at the elevated operating temperatures of printheads employing hot-melt inks. The polyamide resin composition of the present invention has a melt viscosity at 130 °C of less than about 500 centipoise, preferably less than about 250 centipoise, and more preferably less than about 100 centipoise. The polyamide resin composition is solid at room temperature and liquid at the printhead's operating temperature, and so preferably has a melting point within the range of 50 °C and 130 °C. The polyamide resin composition has a low average molecular weight, and preferably a number average molecular weight less than about 2500.

The polyamides of the present invention have the formula:

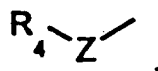


wherein

A is selected from



and



and wherein

R_1 is selected from monovalent C_1 - C_{22} hydrocarbyl;

R_2 is selected from C_2 - C_{36} hydrocarbyl;

5 R_3 is a divalent C_1 - C_{36} hydrocarbyl;

R_4 is selected from monovalent C_1 - C_{22} hydrocarbyl;

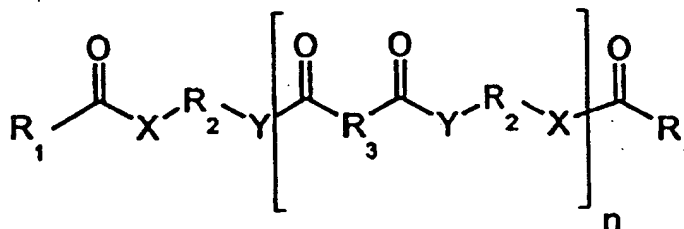
n is an integer from 1 to 10 (to provide from 1 to 10 units), and preferably from 1 to 4 (to provide from 1 to 4 units);

Z is selected from NH and O; and

10 when A is R_4 -Z-, X and Y are independently selected for each unit from (1) X = NH and Y = O; (2) X = O and Y = NH; (3) X, Y = NH; otherwise X and Y are independently selected for each unit from (1) X = NH and Y = O; and (2) X = O and Y = NH.

Thus, the symmetric polyamides of the present invention have the formula:

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The symmetric polyamides of the present invention are prepared by the condensation polymerization reaction of a monoacid, a second reactant selected from aminoalcohols and blends thereof, and a diacid. The relative ratios of
20 monoacid, the second reactant, and the diacid are selected to provide the desired melt viscosity and physical properties. Preferably, the monoacid, the second reactant, and the diacid are reacted together in a molar ratio of about 1.6 - 2.4 to 1.6 - 2.4 to 0.8 - 1.2, respectively. More preferably, the monoacid, the second reactant, and the diacid are reacted together in a molar ratio of about 2 to about 2
25 to about 1; that is, about 2: 2: 1; respectively.

In addition to symmetric polyamides, the polyamide resin compositions of the present invention can optionally include "asymmetric" polyamides having the structure:

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

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Monoacids useful in the practice of the present invention are preferably of the formula



wherein R_1 is selected from monovalent $C_2\text{--}C_{22}$ hydrocarbyl radicals, may be included in the reaction mixture. R_1 can be an alkyl group or can be a hydrocarbyl group including one or more carbon-carbon double bonds. Preferably, R_1 is selected from alkyl chains having from 3 to 22 carbon atoms, aryl chains having from 6 to 22 carbon atoms, alkylaryl chains having from 7 to 22 carbon atoms, and alkylarylalkyl chains having from 8 to 22 carbon atoms. More preferably, R_1 is selected from C_9 to C_{22} hydrocarbyl. Even more preferably, R_1 is selected from C_{16} to C_{22} hydrocarbyl.

Suitable monoacids useful in the preparation of the polyamide include, but are not limited to, acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, nonadecanoic acid, eicosanoic acid, heneicosanoic acid, docosanoic acid, tricosanoic acid, hexacosanoic acid, heptacosanoic acid, octasanoic acid, triacontanoic acid and mixtures thereof.

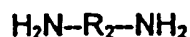
Preferably, an aminoalcohol useful in the present invention is selected from compounds having the formula



wherein R_2 represents divalent $C_2\text{--}C_{36}$ hydrocarbyl. Preferably, R_2 is selected from alkylene chains with up to 36 carbon atoms, cycloalkylene chains from 6 to 36 carbon atoms, divalent aryl radicals, and alkylarylene chains with from 7 to 36 carbon atoms. More preferably, R_2 is divalent linear $C_2\text{--}C_6$ aliphatic.

Suitable aminoalcohols include, but are not limited to, ethanolamine, 4-aminophenol, 1-amino-2-propanol, 3-amino-1-propanol, 2-amino-1-butanol, 4-amino-1-butanol, 5-amino-1-pentanol, and the like.

Preferably, a diamine useful in the present invention is selected from compounds having the formula



wherein R_2 represents divalent $C_2\text{--}C_{36}$ hydrocarbyl or a divalent poly(alkylene oxide) moiety containing between 4 and 36 carbon atoms and from 1 to 17 oxygen atoms. Preferably, R_2 is selected from divalent aliphatic (i.e. alkylene) chains with up to 36

carbon atoms, cycloalkylene chains from 6 to 36 carbon atoms, alkylarylene chains with from 7 to 36 carbon atoms, or poly(ethylene oxide) and poly(propylene oxide) and poly(butylene oxide) moieties having molecular weights between 200 and 400. More preferably, R_2 is divalent linear C_2-C_6 aliphatic.

- 5 Suitable diamines include, but are not limited to, ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 1,2-diamino-2-methylpropane, 1,5-diaminopentane, 2,2-dimethyl-1,3-propanediamine, 1,3-diaminopentane, 1,6-hexanediamine, 2-methyl-1,5-pentanediamine, 1,2-diaminocyclohexane, 1,4-diaminocyclohexane, 1,7-diaminoheptane, 1,8-
- 10 diaminooctane, 2,5-dimethyl-2,5-hexanediamine, meta-xylenediamine, Jeffamine® EDR-148, 1,9-diaminononane, Jeffamine® D-230, 1,10-diaminodecane, 1,8-diamino-p-menthane, 1,8-diaminonaphthalene, isophoronediamine, 1,12-diaminododecane, and mixtures thereof.

- 15 In addition to diamines in which both the amino groups are primary amino, diamines in which one or both of the amino groups is a secondary amino can be employed in the practice of this invention. Similarly, aminoalcohols in which the amine group is a secondary amine can be employed in the practice of this invention. However, the presence of secondary amino groups generally leads to longer reaction times, and produces a product which is softer and tackier. An
- 20 example of a diamine, which may be used in the practice of this invention, is piperazine. Similarly, in addition to aminoalcohols in which the alcohol group is a primary alcohol group, aminoalcohols in which the alcohol group is secondary can be employed in the practice of this invention, although longer reaction times can be expected.

- 25 Diacids suitable for use in the present invention include dicarboxylic acids of the formula:



- wherein R_3 is a divalent C_1-C_{34} hydrocarbyl radical. Preferably, R_3 is a divalent hydrocarbyl chain having from 1 to 34 carbon atoms, and preferably is selected
- 30 from divalent aliphatic chains of 1-34 carbon atoms, divalent cycloaliphatic chains of 3-34 carbon atoms, arylene chains of from 6-34 carbon atoms, alkarylene chains of from 7-34 carbon atoms, and alkarylalkylene chains of from 8-34 carbon atoms.

More preferably, R_3 is selected from divalent branched C_{3-4} aliphatic radicals from C_{3-6} dimer acid, and divalent linear C_6-C_{10} aliphatic radicals.

Suitable diacids useful in the practice of the present invention include, but are not limited to oxalic acid, malonic acid, succinic acid, methylmalonic acid, fumaric acid, maleic acid, acetylene dicarboxylic acid, glutaric acid, ethylmalonic acid, dimethylmalonic acid, methylsuccinic acid, citraconic acid, glutanconic acid, itaconic acid, mesaconic acid, adipic acid, 2,2-dimethylsuccinic acid, 3-methylglutaric acid, hydromuconic acid, pimelic acid, butylmalonic acid, diethylmalonic acid, 2,2-dimethylglutaric acid, 2-ethyl-2-methylsuccinic acid, 3-methyladipic acid, cyclopentanedicarboxylic acid, suberic acid, cyclohexanedicarboxylic acid, isophthalic acid, terephthalic acid, azelaic acid, 5-norbornene-2, 3-dicarboxylic acid, cyclohexylsuccinic acid, benzylmalonic acid, phenylene diacetic acid, phenylsuccinic acid, undecanedioic acid, 3-phenylglutaric acid, 10-decanedicarboxylic acid, traumatic acid, 4-phenylenedipropionic acid, naphthalene dicarboxylic acid, 11-undecanedicarboxylic acid, 12-dodecanedicarboxylic acid, 4-biphenyldicarboxylic acid, diphenic acid, hexadecanedioic acid, dimer acids, and mixtures thereof.

Dimer acids are dicarboxylic acids formed by the reaction of two or more unsaturated fatty acids such as oleic and linoleic acids at elevated temperature and acidic conditions to give a mixture typically including monomeric, dimeric, and higher mer species, and which is subsequently purified by distillation. The preparation of dimer acids is reviewed in R.W. Johnson, et al., "Polyamides From Fatty Acids," *ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING*, Vol. 11 (John Wiley & Sons, New York, 1988), pp. 476-489.

It is preferred that the diacid comprises from about 70 to 100 equivalent percent of dimer acid and from about 30 to 0 equivalent percent of a linear diacid. Linear diacids which can be used in the present invention include sebacic acid, azelaic acid, adipic acid, and 1,10-decanedicarboxylic acid.

Whichever monoacid, second reactant, and diacid are utilized, it is preferable that they be combined in a molar ratios of about 1.6-2.4 moles monoacid: 1.6-2.4 moles second reactant: 0.8-1.2 moles diacid. More preferably, the molar ratios of monoacid, second reactant, and diacid are about 2:2:1, respectively. By using approximately two moles of monoacid for every two moles of second reactant, it has been found that a very low number average molecular

weight polyamide can be produced which effectively contributes to the low melt viscosity useful for the ink compositions of the present invention.

An alternative convention to characterize the relative amounts of monoacid, second reactant, and diacid to employ in preparing the polyamides of the invention is based on reactive equivalents. Monoacids have one reactive equivalent per molecule. The second reactants, diamines and aminoalcohols, have two reactive equivalents per molecule. Diacids have two reactive equivalents per molecule. Thus, it is preferable that the monoacid, second reactant, and diacid be combined in reactive equivalent ratios of about 0.8 - 1.2 equivalents monoacid: 1.8 - 2.2 equivalents second reactant: 0.8 - 1.2 equivalents diacid. More preferably, the reactive equivalent ratios of monoacid, second reactant, and diacid are about 1: 2: 1 respectively.

Yet another convention to characterize the relative amounts of monoacid, second reactant, and diacid to employ in preparing the polyamides of the invention is based on equivalent percents. The total equivalents of amine and alcohol present in the formulation are defined as 100%. The total equivalents of monoacid present in the formulation divided by the total equivalents of amine and alcohol, multiplied by 100, gives the equivalent percent of monoacid present. The total equivalents of diacid (where there are two equivalents per molecule of diacid) present in the formulation divided by the total equivalents of amine and alcohol, multiplied by 100, gives the equivalent percent of diacid present. Thus, it is preferable that the monoacid, second reactant, and diacid be combined such that there are from about 40 to 60 equivalent percent monoacid, 100 equivalent percent second reactant, and 40 to 60 equivalent percent diacid (treating monoacid impurity in the dimer acid as if it were diacid).

Preferably, the hot-melt ink compositions of the present invention are prepared by standard condensation polymerization techniques for reacting, in molar ratio, two moles of monoacid, two moles of second reactant, and one mole of diacid. More preferably, the polyamide resin is prepared by condensing, in a molar ratio, two moles of the monoacid stearic acid ($C_{18}H_{36}O_2$), two moles of the alcoholamine ethanolamine, and one mole of the diacid known as dimer acid (prepared by the polymerization of unsaturated fatty acids available, for example, from tall oil).

Optionally, a fourth reactant selected from monoamines, monoalcohols, and mixtures thereof, the fourth reactant having the formula



wherein R_4 is selected from monovalent C_1 - C_{22} hydrocarbyl radicals, may be included in the reaction mixture, and Z is selected from O and NH. Preferably, R_4 is selected from alkyl chains having from 3 to 22 carbon atoms, aryl chains having from 6 to 22 carbon atoms, alkylaryl chains having from 7 to 22 carbon atoms, and alkylarylalkyl chains having from 8 to 22 carbon atoms. The fourth reactant is preferably substituted for a portion of the second reactant and a portion of the monoacid in the reaction mixture.

The polyamide resin thereby produced in this embodiment of the present invention preferably consists of the condensation reaction product of the fourth reactant (preferably monoamine), monoacid, the second reactant and diacid in a mole ratio of 0.8-1.2 moles fourth reactant: 0.8-1.2 moles monoacid: 0.8-1.2 moles second reactant: 0.8-1.2 moles diacid. Preferably, the molar ratio of fourth reactant to monoamine to monoacid to second reactant to diacid is about 1: 1: 1: 1: 1. This polyamide also affords a hot-melt composition of low viscosity that is solid at room or ambient temperatures and melts at temperatures of from about 60 °C to about 120 °C.

Monoamines useful in the practice of the present invention are preferably of the formula

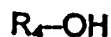


where R_4 is monovalent C_1 - C_{22} hydrocarbyl radical. Preferably, R_4 is C_1 - C_{22} alkyl; more preferably C_{14} - C_{22} alkyl, and still more preferably C_{18} alkyl, that is, stearyl. Specific suitable monoamines include, but are not limited to: methylamine, ethylamine, propylamine, butylamine, amylamine, 1-methoxy-2-aminopropane, hexylamine, stearylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, 1-tetradecylamine, 1-hexadecylamine, octadecylamine, behenylamine and mixtures thereof. Monoamines including unsaturated hydrocarbyl groups can also be employed, although they are less preferred than alkyl monoamines.

Compounds including secondary amino groups can be used in the practice of this invention, however, their use generally affords polyamides which are soft and somewhat tacky, making them less desirable for use as the major component

in a hot-melt printing ink. A minor amount of a slightly tacky resin can be useful however in some ink jet printing ink formulations. Compounds including secondary amino groups generally take longer to react in the formation of the polyamide in comparison to compounds having only primary amino groups, and are therefore less preferred. Similarly, compounds including secondary alcohol groups can be used in the practice of the present invention, although compounds including secondary alcohol groups similarly take longer to react than compounds having only primary alcohol groups, and consequently compounds including primary alcohol groups are preferred.

Monohydric alcohols useful in the practice of the present invention are preferably of the formula



wherein R_4 is monovalent C_1-C_{22} hydrocarbyl radical. Preferably, R_4 is C_1-C_{22} alkyl; more preferably $C_{14}-C_{22}$ alkyl, and still more preferably C_{18} alkyl, that is, stearyl.

Specific suitable monohydric alcohols include, but are not limited to: methanol, ethanol, 1-propanol, 2-propanol, n-butanol, sec-butanol, allyl alcohol, crotyl alcohol, 3-buten-1-ol, 2-methyl-2-propen-1-ol, 2-butyne-1-ol, 3-butyne-1-ol, 1-pentanol, 2-methyl-1-butanol, 1-hexanol, 2-hexen-1-ol, 3-hexen-1-ol, 4-hexen-1-ol, 5-hexen-1-ol, 1-heptanol, 2-heptanol, 3-heptanol, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, 1-tetradecylamine, cetyl alcohol, 11-hexadecen-1-ol, 2,4-hexadien-1-ol, 1-heptadecanol, 1,6-heptadien-4-ol, 1-octadecanol, behenyl alcohol and mixtures thereof.

The condensation polymerization reaction may either be carried out on a step-wise addition basis where, for example, the monoamine is added towards the later part of the reaction, or all the reactants can be mixed together at one time. Preferably the reaction is carried out on a step-wise addition basis because if all the reactants are mixed together at one time there will sometimes occur a sudden and vigorous expansion of the reaction mixture, presumably due to the sudden release of a substantial amount of water formed during the reaction.

In a typical procedure, 100 equivalent percent of a selected aminoalcohol, or mixture thereof with a selected diamine, is charged to a reactor and heated to about 70 °C. With stirring, 50 equivalent percent of a diacid is added dropwise, while the temperature increases to about 130 °C. The temperature is gradually increased from 130 °C to about 160 °C while the bulk of the water of reaction is

distilled. The temperature is then increased to about 220 °C. After substantially all of the water of reaction has been collected, the product mixture is cooled to below 150 °C and 50 equivalent percent of monoamine is added. The reaction mixture is then reheated to about 220 °C until substantially all the water of reaction has been collected. Then a small amount of catalyst, such as phosphoric acid, preferably from about 0.01 to 1.0 percent by weight, is added and the reaction mixture taken under vacuum for 2-3 hours at temperatures between 220-250 °C. This vacuum step removes condensation water and the unreacted volatile starting materials and tends to drive the reaction to completion. The extent of completion of the reaction may be observed by drawing aliquots of the reaction mixture and measuring the acid and/or amine numbers of the reaction mixture and comparing the measured values with those calculated by theory for the fully reacted polyamide resin. The product is then cooled and discharged from the reactor.

To assist the condensation reaction, a catalyst, such as phosphoric acid, may be added to the reaction mixture in catalytic proportion. The catalyst employed in the condensation reaction may be charged to the initial reaction mixture or added slowly just prior to the point at which the reaction rate slows. The preferred concentration of the catalyst in the reaction mixture is within the range of from about 0.001 to 3 weight percent, more preferably from about 0.01 to 1.0 percent by weight of the total materials charged.

Preferably, in order to avoid undue discoloration of the polyamide resin product, the condensation reaction and subsequent formulation mixing is carried out in an inert atmosphere, such as provided by carbon dioxide, nitrogen or argon gases. During the course of the condensation reaction, amidization occurs with the formation of linear oligomeric molecules and water. The formed water is advantageously allowed to distill out of the reaction vessel as the condensation reaction occurs, thus favoring completion of the condensation reaction. Distillation of the water from the reaction mixture may be assisted by allowing a slow stream of inert gas such as nitrogen to be bubbled through or over the surface of the reaction mixture. Although not necessary, an inert organic solvent such as xylene may be added to the reaction mixture in small proportions to assist in the removal of water by azeotropic distillation. Generally, the amount of such inert organic solvent should not exceed about 10 percent by weight of the reaction mixture. The heating of the reaction mixture may be carried out until there is no longer any evolution of

water of condensation, indicating that the polymerization reaction has been completed. The composition is cooled and is ready for incorporation into the hot-melt printing ink compositions.

5 The condensation reaction may be carried out at atmospheric or higher pressures. However, as the end of the condensation reaction is approached, it is advantageous to operate under a slight vacuum, which aids in the removal of byproducts, solvents, condensation water, and unreacted starting materials, thus
10 tending to drive the reaction to completion. Completion of the reaction may be observed by drawing aliquots of the reaction mixture, and measuring the acid and/or amine numbers of the reaction mixture, and comparing the measured acid and/or amine numbers with those calculated by theory for the fully reacted polyamide resin. Generally, polymerization is completed within about 8 hours, depending on the specific reactants employed, the relative proportions of the reactants, et al. Any convenient or conventional reaction vessel can be used to
15 condense the reactants and carry out the polymerization.

The polyamide resins of the present invention are substantially neutral. Their acid and amine numbers are generally each less than 20.

The polyamide resin compositions produced according to the practice of the present invention have relatively low melting points and low melt viscosities.
20 Diluents such as monoamides, bisamides, esters, polyesters and alkanol esters may be added to further lower the melt viscosity. These diluents also may act as solvating agents for the dye or pigment which is responsible for the color of the hot-melt composition. The ink composition is prepared by physically blending together the components, including the polyamide resin composition of the present invention
25 and a suitable colorant, into a substantially homogeneous mixture. The components can be mixed and ground into a finely divided state and then the mixture melted to complete the blending of the components. It has been found that it is preferable to initially melt the polyamide resin and then blend each of the additives into it. The resulting molten mixture can then be readily mixed and cast
30 into an appropriate size and shape upon cooling for use in hot-melt ink-jet printers.

It is necessary that a hot-melt ink be of sufficiently low viscosity at the operating temperatures maintained in the printhead so that the ink can be jetted from the printhead. While hot-melt inks generally exhibit low viscosity with increasing temperature, and thus typically have a desirably low viscosity at some

temperature, the design of the printhead sets one practical limit on the temperature at which the ink can be jetted. It is more difficult and expensive to build printheads which operate at higher temperatures. It is commercially desirable to operate printheads within the temperature range of about 110 °C to 160 °C, with the lower temperatures being generally preferred. Hot-melt inks useful for hot-melt printing have a melting point and a low melt viscosity within the operation temperature of the printhead in order to be "jettable", with a typical viscosity being less than or equal to 500 centipoise at 130 °C, preferably less than or equal to 250 centipoise at 130 °C, and more preferably less than 100 centipoise at 130 °C.

Hot-melt inks are typically comprised of a colorant and a carrier. Desirably, the carrier should dissolve the colorant, be largely transparent when solid, be non-toxic and be stable during long-term heating. The carrier must contribute to the properties needed in the hot-melt ink. These properties include compatibility with the operating conditions of the printhead, e.g., the ink must melt and be at a proper viscosity when subject to the operating temperature of the printhead, and the ink must not corrode the printhead. The ink should contain no volatile components. The carrier should impart to the printed substrate the properties of scuff resistance, resistance to offset, and good adhesion. When printed on transparent substrates, the ink should be rectilinearly light transmissive.

The carrier may comprise more than one component. In order to afford a wide latitude in formulating a hot-melt ink, it is desirable that a potential component have a wide compatibility with other potential components.

The acid number and amine number of the polyamide resin are assessed in a conventional manner. The acid number is calculated as the number of milligrams of potassium hydroxide required to neutralize the free acidity present in one gram of the polyamide resin, while the amine number is calculated as the number of milligrams of potassium hydroxide equivalent to the quantity of acid required to neutralize the free basicity in one gram of the polyamide resin.

The dropping point of the polyamide resin is measured in a conventional manner. Preferably, the polyamide resin has a dropping point of less than about 115 °C.

The following examples are provided to better disclose and teach the hot-melt compositions of the present invention. They are for illustrative purposes only, and it must be acknowledged that minor variations and changes can be made

without materially affecting the spirit and scope of the invention as recited in the claims that follow.

Example I

5 A polyamide resin according to the present invention was prepared as follows: Into a suitable kettle was charged 234.5 g UNIDYME[®] 14 dimer acid (0.820 equivalents, 0.410 moles, UNIDYME 14 is a commercial dimer acid available from Union Camp Corporation of Wayne, NJ and comprises 1% monomeric fatty acid, 96% dimer acid, and about 3% trimer acid) and 50 g
10 ethanolamine (1.64 equivalents, 0.819 moles, ethanolamine (2-aminoethanol) is available from Aldrich Chemical Company of Milwaukee, WI), and 230.9 g stearic acid (0.812 equivalents, 0.812 moles, stearic acid is available from Aldrich Chemical Company of Milwaukee, WI). The reactants were heated under a nitrogen atmosphere at about 180 °C over 8 hours, while water produced in the
15 condensation reaction was collected. The mixture was allowed to cool to room temperature overnight. The next day 3 drops (ca. 0.3 g) of phosphoric acid was added to the reactants and the reaction mixture was heated to 220 °C for about 4 hours and subjected to vacuum (of approximately 2 mm Hg) during the final two hours. The product was then discharged from the kettle.
20 The product was opaque, soft and somewhat tacky, and had a dropping point of 68.5 °C as measured by a Mettler FP83HT Dropping Point Cell connected to a Mettler FP80HT Central Processor. The product had a melt viscosity of 20.1 centipoise as measured at 150 °C on a Brookfield RVTD viscometer running at 30 rpm with a #18 spindle (shear rate of 66 sec⁻¹). The product had an acid number of
25 9.6 and an amine number of 1.0.

Example II

 Example I was essentially repeated, this time substituting equivalent amounts of sebacic acid ($\text{HO}_2\text{C}(\text{CH}_2)_8\text{CO}_2\text{H}$) and dimer acid for the total amount (on an equivalent basis) of dimer acid employed in Example I. The product had a
30 dropping point of 84.1 °C, a melt viscosity at 150 °C of 14.7 centipoise, a melt viscosity at 130 °C of 24.0 centipoise, an acid number of 23.1, and an amine number of less than 1.0. The product was opaque, brittle and very slightly tacky.

Example III

Example I was essentially repeated, this time substituting equivalent amounts of 4-aminophenol and ethanolamine for the total amount (on an equivalent basis) of the ethanolamine employed in Example I. The product had a dropping point of 85.4 °C, a melt viscosity at 150 °C of 30.6 centipoise, a melt viscosity at 130 °C of 57.1, an acid number of 32.9, and an amine number of less than 1.0. The product was opaque, slightly tacky, and soft.

Example IV

Example I was essentially repeated, this time substituting equivalent amounts of ethylenediamine and ethanolamine for the total amount (on an equivalent basis) of the ethanolamine employed in Example I. The product had a dropping point of 112.9 °C, a melt viscosity at 150 °C of 33.5 centipoise, a melt viscosity at 130 °C of 62.5 centipoise, an acid number of 9.6, and an amine number of less than 1.0. The product was almost clear (slightly hazy), not tacky, and hard.

Example V

Example I was essentially repeated, this time using equimolar amounts of dimer acid, monoethanolamine, stearic acid and stearyl amine. The product had a dropping point of 76.1 °C, a melt viscosity at 150 °C of 22.5 centipoise, a melt viscosity at 130 °C of 41.0 centipoise, an acid number of 4.4, and an amine number of less than 1.0. The product was almost opaque, slightly tacky, and soft.

Example VI

Example V was essentially repeated, this time substituting ethylenediamine for the monoethanolamine employed in Example V. The product had a dropping point of 103.9 °C, a melt viscosity at 150 °C of 36.4 centipoise, and acid number of 6.2, and an amine number of less than 1.0. The product was clear and non-tacky.

Example VII

Example VI was essentially repeated, this time substituting an equivalent amount of a dimer diamine for the ethylenediamine. The product had a dropping point of 76.6 °C, a melt viscosity at 150 °C of 28.9 centipoise, a melt viscosity at 130 °C of 54.1 centipoise, and an acid number of 2.0. The product was opaque and very slightly tacky.

Example VIII

Example VI was essentially repeated, this time substituting an equivalent amount of octadecanol for the ethylenediamine. The product had a dropping point

of 103.1 °C, a melt viscosity at 150 °C of 23.7 centipoise, a melt viscosity at 130 °C of 43.6 centipois , an acid number of 7.5 and an amine number of less than 1.0. The product was opaque, very slightly tacky and soft.

5 Various modifications can be made in the details of the various embodiment of the compositions of the present invention, all within the scope and spirit of the invention as defined by the appended claims.

CLAIMS

1. A resin composition comprising a polyamide and useful in the preparation of hot-melt printing compositions, the polyamide being prepared from a reaction mixture selected from (1) reaction mixtures including monoacid, a second reactant selected from aminoalcohols, and blends of aminoalcohols and diamines, and diacid; and (2) reaction mixtures including monoacid, a second reactant selected from diamines, aminoalcohols, and blends of aminoalcohols and diamines, diacid, and a fourth reactant selected from the group consisting of monoamines, monoalcohols, and blends thereof; and the viscosity of the polyamide at 130 °C being less than about 500 centipoise and the number average molecular weight being less than about 2500.

2. A polyamide resin according to claim 1 wherein said polyamide resin is produced by condensation polymerization of a reaction mixture including a monoacid, a second reactant selected from aminoalcohols, and blends of aminoalcohols and diamines, and diacid; said monoacid, said second reactant and said diacid being reacted together in molar ratios of about 1.6 - 2.4 moles monoacid: 1.6 - 2.4 moles second reactant: 0.8 - 1.2 moles diacid.

3. A polyamide resin according to claim 2 wherein said monoacid, said second reactant and said diacid are reacted together in molar ratios of about 2: 2: 1, respectively.

4. A polyamide resin according to claim 1 wherein said polyamide resin is produced by condensation polymerization of a reaction mixture including a monoacid, an aminoalcohol, a diacid, and a monoamine; said monoacid, said aminoalcohol, said diacid, and said monoamine being reacted together in molar ratios of about 0.8 - 1.2 moles monoacid: 0.8 - 1.2 moles aminoalcohol: 0.8 - 1.2 moles diacid: 0.8 - 1.2 moles monoamine.

5. A polyamide resin according to claim 1 wherein said diacid comprises from about 70 to 100 equivalent percent of dimer acid and from about 30 to 0 equivalent percent of a linear diacid.

6. A polyamide resin according to claim 1 wherein said monoacid has the formula $R_1\text{--COOH}$, wherein R_1 is $C_1\text{--}C_{22}$ alkyl.

7. A polyamide resin according to claim 6 wherein R_1 is $C_{14}\text{--}C_{22}$ alkyl.

8. A polyamide resin according to claim 7 wherein R_1 is stearyl.
9. A polyamide resin according to claim 1 wherein said diamine has the formula $H_2N-R_2-NH_2$ wherein R_2 is divalent linear C_7-C_8 aliphatic.
10. A polyamid resin according to claim 1 wherein the diacid has the formula $HOOC-R_3-COOH$ wherein R_3 is selected from the group consisting of divalent branched C_{34} aliphatic radicals derived from dimer acid, and divalent linear C_6-C_{10} aliphatic radicals.
11. A polyamide resin according to claim 1 wherein the fourth reactant has the formula R_4-ZH , wherein Z is selected from O and NH, and R_4 is $C_{14}-C_{22}$ alkyl.
12. A polyamide resin according to claim 1 having a viscosity at 130 °C of less than about 100 centipoise.
13. A polyamide resin prepared by contacting in a reaction mixture:
 - (a) 0.8-1.2 reactive equivalents of a monoacid having the formula R_1-CO_2H where R_1 is monovalent C_1-C_{22} hydrocarbyl;
 - (b) 1.8-2.2 reactive equivalents of an aminoalcohol of the formula H_2N-R_3-OH wherein R_3 represents divalent C_2-C_{36} hydrocarbyl; and
 - (c) 0.8-1.2 reactive equivalents of a dicarboxylic acid of the formula $HOOC-R_2-COOH$, where R_2 is a divalent C_1-C_{34} hydrocarbyl.
14. A polyamide resin according to claim 13 wherein the reaction mixture comprises stearic acid, and ethanolamine and dimer acid.
15. A polyamide resin composition according to claim 13 wherein the monoacid has the formula R_4-NH_2 , wherein R_4 is selected from the group consisting of alkyl chains having from 3 to 22 carbon atoms, aryl chains having from 6 to 22 carbon atoms, alkylaryl chains having from 7 to 22 carbon atoms, and alkylarylalkyl chains having from 8 to 22 carbon atoms,
16. A polyamide resin composition according to claim 13 including a polyamide resin consisting of the condensation reaction product of monoamine, aminoalcohol, diacid and monoacid in a mole ratio of about 1 mole monoamine: 1 mole aminoalcohol: 1 mole diacid: 1 mole monoacid, respectively.
17. A polyamide resin composition according to claim 13 wherein the reaction mixture comprises stearylamine, ethanolamine, dimer acid, and stearic acid.

18. A polyamide resin composition according to claim 13 having a melting point of less than about 115 °C.

19. A polyamide resin composition according to claim 13 having a viscosity at 130 °C less than about 250 centipoise.

20. A hot-melt composition useful in ink-jet printers comprising:

a) a polyamide resin composition including a polyamide, the polyamide being prepared from a reactions mixture selected from (1) reaction mixtures including monoacid, a second reactant selected from the group consisting of aminoalcohols, and blends of aminoalcohols and diamines, and diacid; and (2) reaction mixtures including monoacid, a second reactant selected from the group consisting of aminoalcohols, and blends of aminoalcohols and diamines, diacid, and a fourth reactant selected from the group consisting of monoamines, monoalcohols, and blends thereof; the viscosity of the polyamide at 130 °C being less than about 500 centipoise, the number average molecular weight being less than about 2500; and

b) at least one colorant.

AMENDED CLAIMS

[received by the International Bureau on 6 February 1996 (6.02.96) original claims 1-4, 15-17 and 20 cancelled; original claims 5, 6 and 9-12 amended; new claims 21-25 added: remaining claims unchanged (3 pages)].

5. A polyamide resin according to claim 21 wherein said diacid comprises from about 70 to 100 equivalent percent of dimer acid and from about 30 to 0 equivalent percent of a linear diacid.
6. A polyamide resin according to claim 21 wherein said monoacid has the formula $R_1\text{--COOH}$, wherein R_1 is $C_1\text{--}C_{22}$ alkyl.
7. A polyamide resin according to claim 6 wherein R_1 is $C_{14}\text{--}C_{22}$ alkyl.
8. A polyamide resin according to claim 7 wherein R_1 is stearyl.
9. A polyamide resin according to claim 21 wherein said diamine has the formula $H_2N\text{--}R_2\text{--}NH_2$ wherein R_2 is divalent linear $C_2\text{--}C_8$ aliphatic.
10. A polyamide resin according to claim 21 wherein the diacid has the formula $HOOC\text{--}R_3\text{--COOH}$ wherein R_3 is selected from the group consisting of divalent branched C_{34} aliphatic radicals derived from dimer acid, and divalent linear $C_6\text{--}C_{10}$ aliphatic radicals.
11. A polyamide resin according to claim 21 wherein the fourth reactant has the formula $R_4\text{--}ZH$, wherein Z is selected from O and NH, and R_4 is $C_{14}\text{--}C_{22}$ alkyl.
12. A polyamide resin according to claim 21 having a viscosity at 130 °C of less than about 100 centipoise.
13. A polyamide resin prepared by contacting in a reaction mixture:
 - (a) 0.8-1.2 reactive equivalents of a monoacid having the formula $R_1\text{--CO}_2H$ where R_1 is monovalent $C_1\text{--}C_{22}$ hydrocarbyl;
 - (b) 1.8-2.2 reactive equivalents of an aminoalcohol of the formula $H_2N\text{--}R_3\text{--OH}$ wherein R_3 represents divalent $C_2\text{--}C_{36}$ hydrocarbyl; and

(c) 0.8-1.2 reactive equivalents of a dicarboxylic acid of the formula $\text{HOOC}-\text{R}_2-\text{COOH}$, where R_2 is a divalent C_1-C_{34} hydrocarbyl.

14. A polyamide resin according to claim 13 wherein the reaction mixture comprises stearic acid, and ethanolamine and dimer acid.

18. A polyamide resin composition according to claim 13 having a melting point of less than about 115°C .

19. A polyamide resin composition according to claim 13 having a viscosity at 130°C of less than about 250 centipoise.

21. A polyamide resin composition for use in hot-melt printing inks, said polyamide resin comprising the reaction product of a condensation polymerization of a reaction mixture selected from the group consisting of (1) reaction mixtures consisting essentially of (a) a monoacid, (b) a diacid, and (c) an aminoalcohol, and (2) reaction mixtures consisting essentially of (a) a monoacid, (b) a diacid, (c) a third component selected from the group consisting of (i) diamines, (ii) aminoalcohols, and (iii) mixtures thereof, and (d) a fourth component selected from the group consisting of (i) monoamines, (ii) monoalcohols and (iii) mixtures thereof; said polyamide resin having a viscosity of less than about 500 centipoise at 130°C and a number average molecular weight less than about 2500.

22. A polyamide resin according to claim 21, wherein the mole ratio of reaction mixture (1) is 1.6-2.4 moles monoacid: 0.8-1.2 moles diacid: 1.6-2.4 moles third component.

23. A polyamide resin according to claim 22, wherein the mole ratio of reaction mixture (1) is 2 moles monoacid: 1 mole diacid: 2 moles third component.

24. A polyamide resin according to claim 21, wherein the mole ratio of reaction mixture (2) is 0.8-1.2 moles monoacid: 0.8-1.2 moles aminoalcohol: 0.8-1.2 moles diacid: 0.8-1.2 moles monoamine.

25. A hot-melt ink-jet ink composition, comprising:

- a) a polyamide resin comprising the reaction product of a condensation polymerization of a reaction mixture selected from the group consisting of (1) reaction mixtures consisting essentially of (a) a monoacid, (b) a diacid, and (c) an aminoalcohol, and (2) reaction mixtures consisting essentially of (a) a monoacid, (b) a diacid, (c) a third component selected from the group consisting of (i) diamines, (ii) aminoalcohols, and (iii) mixtures thereof, and (d) a fourth component selected from the group consisting of (i) monoamines, (ii) monoalcohols and (iii) mixtures thereof; said polyamide resin having a viscosity of less than about 500 centipoise at 130°C and a number average molecular weight less than about 2500; and
- b) at least one colorant.

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08G 69/26

US CL : 528/340, 343, 367, 335, 339.3; 106/20R, 20D

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/340, 343, 367, 335, 339.3; 106/20R, 20D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,218,351 (RASMUSSEN) 19 August 1980, see entire document.	1-20

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

Special categories of cited documents:	
A document defining the general state of the art which is not considered to be part of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
E earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O document referring to an oral disclosure, use, exhibition or other means	*A* document member of the same patent family
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

14 NOVEMBER 1995

Date of mailing of the international search report

27 DEC 1995

 Name and mailing address of the ISA/US
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European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 30 2984

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A.D	US 5 041 161 A (COOKE THEODORE M ET AL) 20 August 1991		C09D11/00
A	EP 0 556 649 A (DU PONT) 25 August 1993	1.2	
A	WO 96 10051 A (UNION CAMP CORP) * page 3, line 16 - line 20 * * page 9, line 26 - line 33 * * page 14, line 4 - line 9 *	1.2	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C09D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		20 January 1998	Miller, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background C : non-written disclosure P : intermediate document 1 : theory or principle underlying the invention E : earlier patent document but published on or after the filing date D : document cited in the application L : document cited for other reasons 3 : member of the same patent family, corresponding document			

EP 0 805 192 A3 (1998-01-20)